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(54) Elastomeric silicone finishes and method of preparing same.

(57) An elastomeric silicone finish is prepared from a silicone system comprising a blend of silanols and crosslinkable silicone intermediates. The blend is applied to the desired substrate and thereafter catalyzed and cured to obtain an elastomeric finish.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a silicone system which provides an elastomeric silicone finish and methods of preparation thereof. The silicone system is prepared from a blend of silanols and crosslinkable silicone intermediates. This silicone system can be used in combination with other known finishing agents.

2. Description of the Prior Art

Silicone products have been used extensively in the textile industry for more than twenty years as water repellents, antifoams, lubricants, softeners and the like. The most important silicone products have been dimethylpolysiloxane, used as a softener, and methylhydrogenpolysiloxane, used as the base for silicone water repellents.

These silicone products, and others, have advantages over hydrocarbon compounds, paraffin waxes and fatty acid waxes, especially in regards to processing and the ultimate properties of the treated materials. Because of these advantages organosilicon polymers as textile chemicals were explored, resulting initially in U.S. Patent No. 2,891,920 which taught the manufacture of emulsion polymerized dimethyl polysiloxanes.

Some ten years later Weyenberg published a written reference to organosilicon polymers in

textile chemicals. Journal of Polymer Science, Part C, No. 27 (1969). And more recently, the specific application of these silicone polymers as a textile finish has been made by Rooks in Textile Chemist and Colorist, Vol. 4, No. 1, Jan. 1972. The Rooks article specifically referred to the use of silanol endblocked dimethylpolysiloxane emulsion polymers with monomeric methyltrimethoxy silanes as the crosslinker and an organo tin catalyst. The Rook article noted that the use of these ingredients in fortifying or improving the durable press performance of polyester/cellulosic blends was its most important application. However, this technology proved commercially unacceptable because of its lack of consistency under mill conditions and the occurrence of silicone spots on the fabric.

Recently, an elastomeric silicone system has been introduced as a textile finish. This system is reported to impact improved resilience and stretch, shape recovery and dimensional stability to knitted and stretched woven fabrics. This silicone system consists of three emulsion components, the components are a high molecular weight silanol fluid with a dimethylmethylhydrogen fluid correactant and a zinc 2-ethylhexonate catalyst. The system is in emulsion form, which limits the ability of formulators to add value to the component materials and is subject to critical operating conditions which if not met could result in a dangerous evolution of hydrogen.

Despite these recent advances there continues a need for a silicone system that provides

a better elastomeric finish that is easier to employ and which acts as a softener by itself or can be used as a component in a durable resin bath.

5 Additionally, the silicon system must be stable and impart formulation latitude so as to be acceptable across the spectrum of mill operations. Finally, it is important that the silicone system be easily catalyzed and preferably employ the same catalyst as found in a typical durable press resin bath.

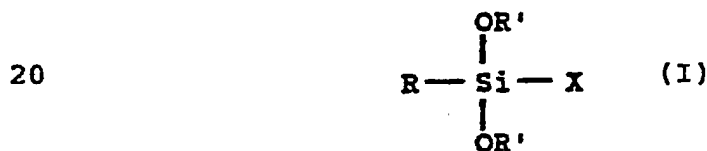
10 Summary of the Invention

A silicone system prepared from a blend of silanols and crosslinkable silicone intermediates. Said silicon system being capable to form a  
15 elastomeric film which functions as a softener, a water repellant and imparts resiliency and extensibility. Furthermore, the present silicone system can not only be used alone, but also finds great utility as a component in a durable press  
20 resin bath. This silicone system is remarkably stable and provides a great amount of formulation latitude in textile finishes. Additionally, the elastomeric finish has been shown to provide a performance which can be varied by the degree of  
25 functionality or molecular weight of the crosslinkable silicone intermediate. Catalysis for the present system is much less critical than previous systems in that any variety of acid catalyst can be employed in small amounts. Of  
30 particular advantage is the fact that the present silicone system is catalyzed by any conventional durable press resin catalyst, thereby eliminating the need for a two-catalyst system.

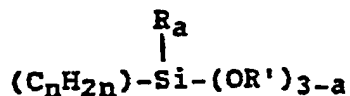
Detailed Description of the Invention

In accordance with the present invention, there is provided a silicone system suitable to provide an elastomeric finish upon curing. The silicone system is prepared by reacting a silane and a silanol to obtain a crosslinkable silicone intermediate which is thereafter reacted with a second silanol to obtain a silicone composition which, when catalyzed, can be used as an elastomeric finish or coating for textiles, paper, cellulose materials, glass fibers and mineral substrates. The elastomeric finish or coating provides a film which is soft, resilient and durable. It is also believed that this film may impart lubricity and adhesive release properties.

The silanes which are suitable for use in preparing the crosslinkable silicone intermediate contain those generally represented by the formula:



wherein R is individually hydrogen, OR' or a substituted or unsubstituted hydrocarbon radical containing from 1 to 12 carbon atoms inclusive, preferably 1 to 3 carbon atoms and most preferably a methyl group, and X is R, OR' or

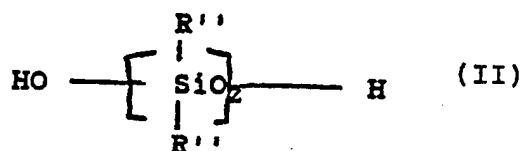


and R' is individually a hydrocarbon radical containing from 1 to 6 carbon atoms, preferably from

1 to 3 carbon atoms. R' can be the same or different. The value of n is 1, 2, or 3 and preferably 2 and a is zero, 1 or 2. It is necessary that the silane contain at least 2 and preferably 3 alkoxy groups in order to provide a suitable crosslinkable silicone intermediate.

Illustrative of such silanes include, but are not necessarily limited to, methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, methylpentamethoxydisilylethane, tetraethoxysilane, cyclohexyltriethoxysilane, and methyltripropoxysilane. tetraethoxysilane, cyclohexyltriethoxysilane, and methyltripropoxysilane.

Suitable silanols which can be used in the preparation of the crosslinkable silicone intermediate are these represented by the formula:



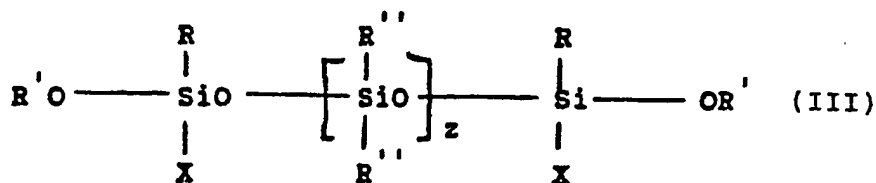
wherein R' is individually a hydrocarbon radical of from 1 to 12 carbon atoms inclusive and may be cyclic or noncyclic, saturated or unsaturated, branched or nonbranched, substituted or unsubstituted and wherein z has a value of from 10 to 500 and preferably having a value of 15 to 150. The commercially available silanols are predominately disilanols, but may contain small amounts of mono- and poly-silanols.

For the purposes of the present invention, it is preferred that the silanol be a dihydroxy endblocked dimethyl polysiloxane.

The reaction between the silane as represented by Formula I and the silanol as represented by Formula II takes place under conditions which are not strictly critical.

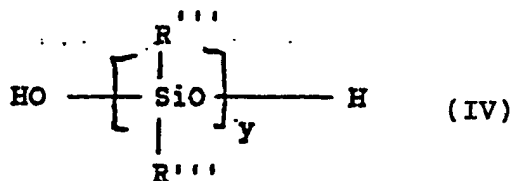
- 5 Broadly, however, the reaction will occur within a temperature range of from 70° to 120°C. Higher and lower temperatures may be employed but are not preferred. A nitrogen purge to remove any alcohol byproducts and unreacted silane ester is
- 10 recommended, although it is not critical to the reaction. The reaction product is then heated at reduced pressure to remove all volatile products. Along these lines, time and temperature will affect the reaction rate but are also not strictly
- 15 critical. What is required in determining reaction conditions are those conditions necessary to obtain a condensed product. The molar ratio of silane to silanol should, at a minimum, be stoichiometrically equivalent, which requires that there be 2 moles of
- 20 silane per mole of silanol to get a double end-blocked crosslinkable silicone intermediate. No known adverse effect is believed to exist, however, when single end-blocked crosslinkable silicone intermediates are obtained.
- 25 It is very important that when the reaction is run only one of the alkoxy groups is removed. To accomplish this specific catalysts are highly recommended. Illustrative of such catalysts which can accomplish this feat are potassium carbonate
- 30 sodium methoxide and potassium acetate preferably potassium carbonate.

The resultant crosslinkable silicone intermediate is generally represented by the formula:



wherein X, R, R' and R'' and z are all as previously defined.

The crosslinkable silicone intermediate represented by Formula III is subsequently mixed with a second silanol to obtain the blend which will subsequently be catalyzed and cured. Suitable silanols for this subsequent step are those of the general formula:



wherein R''' individually has the same designation as that previously set forth for R'' and wherein y equals 185 to 3500 preferably 750 to 3500. It may be possible to employ silanols where y is greater than 3500, but such silanols are not preferred due to processing difficulties.

It should be pointed out that the silanol of Formula II and the silanol of Formula IV can be interchanged. Although this will increase the viscosity of the crosslinkable silicone intermediate, it is believed to be useful for the purposes of the present invention. If such



interchanges do occur, it will be necessary when blending the crosslinkable silicone intermediate with the subsequently added silanol to use a ratio of from 10 parts to 75 parts by weight of the crosslinkable silicone intermediate for every 90 to 25 parts by weight of the subsequently added silanol respectively.

In the event the interchange previously mentioned does not occur the weight ratio of crosslinkable silicone intermediate to subsequently added silanol should be from 10 to 50 parts by weight of the crosslinkable silicone intermediate to 90 to 50 parts by weight of the subsequently added silanol respectively.

The selection of a value for z and y in the silanols represented by Formulas II and IV respectively is made to meet the specific requirements in performance properties, such as flexibility, resiliency and durability, of the ultimate elastomeric finish. The lower the value of z and/or y, the more brittle and less elastic the ultimate finish will be, conversely the higher the value of z and/or y, the more elastic the ultimate finish will be. In this manner formulators can with ease and convenience control the finish applied to the end products.

In the normal application of a finish, such as a textile finish, the crosslinkable silicone intermediate and the second silanol are preferably emulsified. This, however, is not a critical limitation insofar as nonemulsified blends of the crosslinkable silicone intermediate and silanol in

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Curing is accomplished by any of a variety of methods commonly known to those skilled in the art. A curing method commonly employed is a heating oven whereby the finish is cured onto a desired substrate.

5 In one embodiment of this invention, treatment of the textile material with the elastomeric finish of the present invention and treatment with a durable press resin (also known as  
10 "creaseproofing agent" or "textile resin") are carried out together, i.e. in the same bath. The durable press resins are known in the art and include aminoplast resins, epoxides, aldehydes, aldehyde derivatives, sulfones and sulfoxides.  
15 Aminoplasts are preferred durable press resins as they are relatively inexpensive. Suitable durable press agents are disclosed in "Crease-proofing Resins for Wash-and-Wear Finishing" by A. C. Nuessle, Textile Industries, Oct. 1959, pp. 1-12.  
20 Typical aminoplast durable press resins include the urea-formaldehyde condensates, e.g. methylolated ureas and alkyl ureas; melamine-formaldehyde condensates, e.g. tri, tetra and penta methylol and methoxymethyl melamines,  
25 ~~etc.~~; alkylene ureas, e.g. dimethylol ethylene or propylene urea, dihydroxydimethylol ethylene urea and various alkoxymethyl derivatives thereof; carbamates, e.g. dimethylol alkyl and alkoxyalkyl carbamates, ~~etc.~~; formaldehyde-acrolein condensation  
30 products; formaldehyde-acetone condensation products; alkylol amides, e.g. methylol formamide, methylol acetamide, ~~etc.~~; alkylol acrylamides, e.g.

the presence of a catalyst will work. When an emulsion system is employed the emulsifier can be nonionic, cationic or anionic, preferably a nonionic emulsifier is used. Exemplary of nonionic emulsifiers include, but are not limited to, alkylphenol ethoxylates, primary and secondary alcohol ethoxylates, polyoxyethylene lauryl ethers. Exemplary of the anionic emulsifiers are alkyl benzene sulfonates, sodium lauryl sulfate.

5

10 Exemplary of the cationic emulsifier is trialkyl ammonium chloride.

The elastomeric finish is prepared by applying to the substrate, be it textile, paper, fiberglass or other, a blend or emulsion together with catalyst and, optionally, any other suitable finishing component and thereafter curing the coating onto such surface. Suitable catalysts which can be added to the blend of crosslinkable silicone intermediate and second silanol include those commonly referred to as acid catalysts.

15

20 Illustrative of such catalysts include, but are not necessarily limited to, the metal salts of strong acids, e.g. zinc nitrate, aluminum sulfate, zirconium acetate or zinc sulfate; metal halides, e.g. zinc chloride, magnesium chloride, aluminum chloride; metal soaps, e.g. zinc-2-ethylhexoate, dibutyltin dilaurate or dibutyltin diacetate; non-polymeric anhydrides, e.g. tetrapropenyl succinic anhydride; and butyl acid phosphate. The catalyst should preferably be added to the blend and/or emulsion and thus would not be present when the emulsion or blend is made to obtain optimum shelf life.

25

30

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N-methylol methacrylamide,  
N-methylol-N-methylacrylamide, N-methylol  
methylene-bis(acrylamides), methylen bis(N-methylol  
acrylamide), ~~etc.~~; diureas, e.g. trimethylol and  
tetramethylol acetylene diureas, etc.; triazones,  
5 e.g. dimethyl N-ethyltriazone,  
N,N'-ethylenebis(di-methylol triazone) and urons,  
e.g. dialkoxymethyl uron,

Typical epoxide durable press resins  
include the diglycidyl ethers of polyols such as  
10 ethylene glycol diglycidyl ether and diepoxides such  
as vinyl cyclohexene dioxide. Typical aldehyde  
creaseproofing agents include formaldehyde, glyoxal  
and alpha-hydroxypivaldehyde. Typical aldehyde  
derivative creaseproofing agents include  
15 2,4,6-trimethylol phenol, tetramethylol acetone,  
diethylene glycol acetal and pentaerythritol bis  
acetal.

When the durable press resin and the  
elastomeric finish of the present invention are  
20 applied to the textile material from a single bath,  
a cure catalyst for the durable press resin is  
generally employed. The choice of catalyst is  
governed by the particular durable press resin. By  
way of illustration, catalysts such as magnesium  
25 chloride, zinc chloride, zinc nitrate, zirconium  
acetate, and amine hydrochlorides can be used with  
aminoplasts. Moreover, the catalyst suitable for  
curing the durable press resin will also cure the  
elastomeric finish. The cure of the durable press  
30 resin is usually effected at an elevated temperature  
(e.g. from 150°C to 175°C) and the durable press

resin and the elastomeric finish of the present invention can thus conveniently be simultaneously cured.

5 The treatment of this invention can be employed in conjunction with any other treating steps and treating materials which are conventionally employed in the textile finishing art.

10 Whereas the exact scope of the instant invention is set forth in the appended claim, the following specific examples illustrate certain aspects of the present invention and, more particularly, point out methods of evaluating the same. However, the examples are set forth for illustration only and are not to be construed as  
15 limitations on the present invention except as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

EXAMPLES

- 20 I) Fabric Identification (Test Fabrics Inc., Middlesex, NJ)
- A) 100% texturized polyester double knit jersey, style 720
- 25 B) 100% bleached cotton single knit, sport shirt weight, style 459
- C) 50/50 = Polyester/cotton single knit, tubular, style 7421
- 30 D) 65/35 = Polyester/cotton woven fabric, Type 190, 3 oz./yd<sup>2</sup>

35 The procedural evaluations were run in accordance with the following AATCC and ASTM test methods.

To a 1000 ml. 3 necked round bottomed flask equipped with a magnetic agitator, a thermometer fitted with a Therm-O-Watch regulator, an inlet tube for nitrogen and a distillation column packed (18") 457 mm with (1/4") <sup>6.35 mm</sup> glass helices and fitted with a distillation head, receiver and vent to the hood via - 80°C cold traps, there was charged:

503 g silanol endblocked poly(dimethyl siloxane) having the following properties; wt% OH: 1.69, viscosity 54.1 <sup>mPa.s</sup> (cs.) at 25°C; 81.6 g MeSi(OMe)<sub>3</sub> at 99.7% purity; 4.4 g pulverized K<sub>2</sub>CO<sub>3</sub> anhydrous. The system was heated to 85°C with agitation and (0.2 ft<sup>3</sup>) <sup>5.66 m<sup>3</sup></sup> H<sub>2</sub>/h. until 1 mole ethanol per mole of MeSi(OMe)<sub>3</sub> charged was removed. Treated 18 hours at 90°C with (0.5 ft<sup>3</sup>) 14.15 m<sup>3</sup> N<sub>2</sub>/h purge. The crude reaction product was then vacuum stripped at 100°C (0.2 mm) <sup>0.266 mbar</sup> to remove all volatiles. The compound was refined by pressure filtration through a 1-2 μm pad.

The 'MD<sub>27</sub>M' compound had the following properties:

	Viscosity cs. @ 25°C	30.0
	25	
	n <sub>D</sub>	1.4013
25	Wt% methoxy:	
	found	5.3
	calculated	5.8
	Residual silanol	<200 ppm
30	IR Spectroscopy: Spectrum consistent with anticipated structure showing disappearance of silanol absorption and appearance of SiOMe at 2840 cm <sup>-1</sup> .	

II) Test Procedures

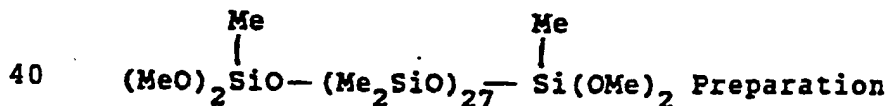
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- 5                   A) Evaluation of Wettability, AATCC  
Method 79-1979
- 10                   B) Elmendorf Tear Resistance, ASTM  
Method D-1424-75
- 15                   C) Conditioning Textiles for  
Testing, ASTM Method D-1776-79
- 20                   D) Applicator: Werner Mathis Padder,  
Model VF-9779
- 25                   E) Wash Cycle  
Kenmore Machine Model 29601  
4# Load  
95 g . A2 TC2 Detergent  
124/Cycle  
Medium water level  
Wash/rinse cycle = (120°F/105°F) 49/40°C
- F) Dry Cycle  
Kenmore Dryer, Model 7218601W  
25 min @ "Normal" setting

30                   The invention can be used for the  
preparation of a remarkably stable emulsion of two  
reactive intermediates which when catalyzed produced  
a crosslinked network which encapsulates or reacts  
with textile, cellulosic, glass fiber, mineral  
substrates. Crosslinking is achieved via water  
evaporation and a short elevated temperature  
catalytic cure.

Experimental

Example I



Gel Permeation Chromatogram: Molecular weight **0129074**  
distribution in full agreement relative to  
starting silanol endblocked fluid.

5 Example II

Additional examples of polyalkoxy  
endblocked dimethyl silicones were prepared in a  
manner essentially identical to that described in  
Example I.

10 Table I summarizes all methoxyendblocked  
silicones prepared and their properties. Table II  
lists the reagents to prepare these compounds. The  
stoichiometries employed are calculated on the basis  
of 2 moles of polymethoxy silane per mole of silanol  
15 fluid. In the cases where  $\text{MeSi(OMe)}_3$  was used, a  
20-50% excess was employed to compensate for  
volatility losses.



TABLE I  
Polymethoxy Endblocked Dimethyl Silicones and Their Properties

CSI (a) Code No.	Compound Formula	Visc. b	25 n <sub>D</sub>	wt %	
				Methoxy Found	Content Calculated
A	'MD <sub>27</sub> M'	30	1.4013	5.3	5.8
B	"MD <sub>27</sub> M"	72	1.4071	9.2	10.1
C	'MD <sub>112</sub> M'	195	1.4032	1.3	1.5
D	"MD <sub>112</sub> M"	380	1.4045	2.7	2.8
E	'MD <sub>112</sub> M'	510	1.4046	---	--

Residual silanol content in all preparations = less than 200 ppm.

(a) CSI - crosslinkable silicone intermediate

(b)  $\eta_{inh}^{25}$  in (cps) at room temperature

TABLE II

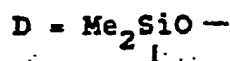
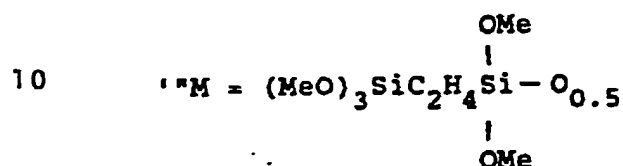
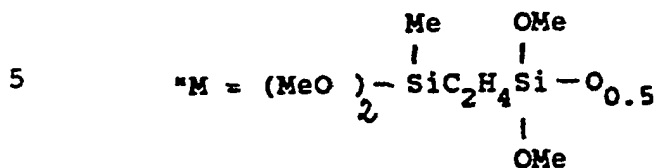
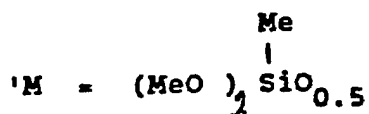
Reagents Used to Prepare Polymethoxyendblocked Dimethyl Silicones

CSI Code No.	Compound Formula	K <sub>2</sub> CO <sub>3</sub> g	Silane		Silanol Fluid	
			g	Composition	g	Visc. (cps.) wt% OH
A	'MD <sub>27</sub> M'	4.4	81.6	Me-Si(OMe) <sub>3</sub>	503	54.1 1.69
B	"MD <sub>27</sub> M"	4.7	127	$\begin{array}{c} \text{Me} \\   \\ (\text{MeO})_2\text{SiC}_2\text{H}_4\text{Si(OMe)}_3 \end{array}$	503	54.1 1.69
C	'MD <sub>112</sub> M'	0.65	4.9	MeSi(OMe) <sub>3</sub>	103.8	144 0.75
D	"MD <sub>112</sub> M"	1.1	6.35	$\begin{array}{c} \text{Me} \\   \\ (\text{MeO})_2\text{SiC}_2\text{H}_4\text{Si(OMe)}_3 \end{array}$	103.8	144 0.75
E	'MD <sub>112</sub> M'	0.5	6.75	(MeO) <sub>3</sub> SiC <sub>2</sub> H <sub>4</sub> Si(OMe) <sub>3</sub>	103.8	144 0.75

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Formula Code:

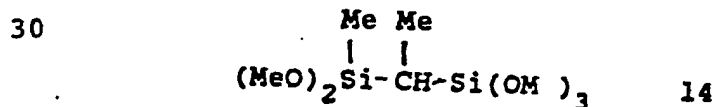
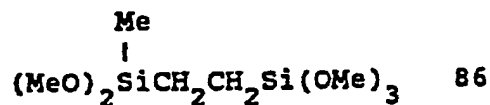


silane, was produced by the Pt catalyzed reaction of  
 $\text{MeSiHCl}_2$  with  $\text{ViSi(OMe)}_3$ , esterified with  
 20 methanol and refined via distillation. The compound  
 has the following properties:

Boiling Point 55°C(0.3 mm Hg) 0.4 mbar

25  
 $n_D$  1.4104

25 Isomer ratio (wt%):



Example III

Preliminary crosslinking studies were conducted by casting acid catalyzed dilute solutions and emulsions of the crosslinkable silicone intermediates (CSI) with and without blends of silanol fluids having viscosities of 1,000-50,000 mm<sup>2</sup>/s (cs.) in laboratory test aluminum cups. In all cases acid catalysis was required for crosslinking to occur. Butyl phosphoric acid (BPA) is highly effective since it is compatible both in oil and water phases. The best elastomeric films were obtained when silanol fluids were admixed with the CSI in ratios of 25/75, 50/50 and 75/25. When the CSI fluid itself was tested a highly crosslinked, friable silicone film was obtained that was deemed unsatisfactory as a textile elastomeric finish.

Concentrated nonionic emulsions of CSI and CSI/silanol fluid blends were prepared using the following materials/procedures.

There was mixed 35.0 g of CSI/silanol fluid slowly into a solution of 1.75 g of a nonionic surfactant composed of a blend of polyoxyethylene lauryl ethers and 1.75 g H<sub>2</sub>O in a plastic beaker. After mixing well 61.35 g water were added until the emulsion was prepared. The emulsion was stabilized by adding 0.1 g. 37% formalin solution and 0.05 g NaHCO<sub>3</sub>. The pH was adjusted to 5.5 with acetic acid. This 35% active emulsion was diluted with tap water to provide dilute test solutions.

The effect of temperature on crosslinking emulsions of 15-50% CSI/85-50% silanols respectively to provide elastomeric films gave the following

results when 2% BAP catalyst (based on silicon  
 solids) was employed. Emulsions comprised of 15/85  
 and 25/75 mixtures of CSI Code A and 20,000 (cstk) mm<sup>2</sup>/s  
 silanol gave elastomeric films when contacted 2 days  
 5 at 25°C, 5 hours @ 50°C or 4 hrs @ 100°C. Films from  
 50/50 mixtures on standing 2 days at 25°C gave an  
 elastomeric film. At 50°C the 50/50 mixture film  
 was dry and after 4 hours at 100°C, we observed a  
 friable dry film showing excessive crosslinking.  
 10 Similarly, a 15/85 blend of Polymethoxy/8,000 (cs.) mm<sup>2</sup>/s  
 silanol fluid respectively gave elastomeric films  
 when treated at the 3 temperature/time conditions.  
 The results clearly show how elastomeric films can  
 be produced from broad mixture ranges of CSI with  
 15 silanol fluids of 8,000 - 20,000 (cstk.) mm<sup>2</sup>/s.

Film forming properties of the liquid CSI  
 were demonstrated by preparing 20% solutions of CSA  
 Code C and CSI Code E in tetrahydrofuran and  
 catalyzing with 5% butyl acid phosphate based on  
 20 silicone. On standing overnight, the solvent  
 evaporated leaving a film via a crosslinking  
 mechanism. Accelerated cure rates were demonstrated  
 via 1/2 hr treatment at 80°C. Blends comprised of  
 25/75, 50/50, and 75/25 CSI with silanol fluids  
 (1,000-8,000 (cs.) mm<sup>2</sup>/s) similarly gave films on standing  
 25 at ambient conditions. A BAP catalyzed silanol  
 control remained fluid showing no propensity for  
 film forming.

#### 30 Example IV

Elastomeric properties were imparted to a  
 variety of fabrics by treatment in a model textile  
 bath which consisted of:

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2.85 g 35% silicone emulsion (as p r  
Example III)

0.10 g butyl acid phosphate (10% in  
wat r)

5 97.05 g distilled water

Applications conditions were adjusted to  
achieve 100% fabric wet pick up which upon drying  
gave 1.0 wt% silicone deposited on the fabric. The  
dry fabric was cured for 1.5 minutes at 171°C.

10 Silicone durability on the fabric was  
determined by washing five times in a 0.15 wt%  
detergent (AATCC #124) solution at <sup>49° C</sup>(120°F) for 30  
minutes then rinsing at 105°C. Prior to physical  
property measurements all fabrics were conditioned  
15 at 50% relative humidity and (70°F.) 21° C.

Bleached 100% cotton knit, sport shirt  
weight, style 459 when treated with CSI/silanol  
fluid mixture gave durable improvements in  
dimensional stability and tear strength relative to  
20 the untreated control. Table III clearly shows  
linear shrinkage or gain has been diminished by 50%  
and furthermore, tear strength has been increased  
15-20% even after 5 launderings.

TABLE III  
100% Cotton Knit treated with CSI/Silanol Fluid Blends

<u>Silicone Bath Components</u>		<u>Dimensional Stability, % after 5 launderings</u>		<u>Tear Strength (Grams) after 5 washes</u>			
<u>CSI (Code)</u>	<u>Silanol Fluid (Viscosity) (a)</u>	<u>course</u>	<u>wale</u>	<u>initial</u>	<u>course</u>	<u>wale</u>	<u>wale</u>
C	8,000	+12.3	-11.2	2200	3000	2100	3000
D	8,000	+9.8	-11.8	2100	3000	2200	3000
C	20,000	+9.6	-10.4	2100	3000	2200	3000
D	20,000	+9.9	10.6	2100	3100	2100	3100
D	1,000	+10.1	-10.6	2200	3100	2200	2900
---	---	+17.5	22.0	2500	2600	2300	2500

(a)  $\frac{\text{mPa}\cdot\text{s}}{(\text{cps})}$  at room temperature

Example V

100% texturized polyester doubl knit jersey, style 720 (Test Fabrics, Inc., Middlesex NJ) was similarly treated with the same finishing bath compositions used in Example IV. Improvements (17-20%) in durable tear strength were measured after 5 launderings. Refer to data in Table IV. It is to be noted that 100% polyester is dimensionally stable.

TABLE IV100% Texturized Polyester Knit

	Silicone Bath Components		Tear Strength (grams)			
	CSI Code	Silanol Fluid, Visc. (a)	Initial		5 washes	
			Course	wale	course	wale
20	C	8,000	2200	3000	2100	3000
	D	8,000	2100	3000	2200	3000
25	C	20,000	2100	3000	2200	3000
	D	20,000	2100	3100	2100	3100
	D	1,000	2200	3100	2200	2900
	--	---	2500	2600	2300	2500

(a) mPa·s  
(cps) at room temperature

Example VI

This example illustrates the improved tear strength achieved by treating 50/50 polyester/cotton



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single knit, tubular, Styl 7421 with a 1% silicone  
actives from treating emulsions comprised of 25  
parts CSI C de B CSI/75 parts 8.000<sup>mpa.s</sup>(cps) silan 1.  
For completeness of data, three catalysts were  
5 individually tested and comparative data are  
recorded in Table IV after fabric washing 3 times.  
The bath components are listed below.

<u>Components</u>		<u>Parts by Weight</u>			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
10	35% Silicone Emulsion	2.9	2.9	2.9	2.9
	BAP (10% in Water)	-	0.2	-	-
	Zn(NO <sub>3</sub> ) <sub>2</sub> (25% in H <sub>2</sub> O)	-	-	0.4	-
	Zr(OAC) <sub>2</sub> (25% in H <sub>2</sub> O)	-	-	-	0.4
15	Water	97.1	96.9	96.7	96.7

Table V also shows Lewis acids are  
effective curing catalysts retaining 80-90% of the  
applied silicone relative to 60% retention for the  
20 noncatalyzed control. The silicone loss before and  
after washing was determined via atomic absorption  
for silicon. Table V also shows significant  
improvements in durable tear strength with up to 30%  
increase in the fill and 90% increase in warp  
25 directions.

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TABLE V

CATALYST	Silicone % Loss After 3 Washes	Tear Strength, grams			
		Initial course	wale	3 wash course	s wale
5 Control X (Silicone, no catalyst)	38	2600	3000	2500	3100
Butyl Acid Phosphate + silicone	19	2500	3100	2400	3100
10 Zn(NO <sub>3</sub> ) <sub>2</sub> + silicone	10	2600	3000	2600	3000
Zr(OAC) <sub>2</sub> + silicone	22	2500	2900	2600	3100
15 Control Y (No Silicone, no catalyst)	--	2300	2100	2000	1600

Conditions

- 20 1) Fabric: 50/50 = Polyester/cotton, single knit tubular
- 2) Silicone Applied: 25/75 = CSI Code B polymethoxy fluid/L9000(8000), 35% Emulsion.

25 Example VII

This example illustrates the remarkable stability of CSI/silanol fluid emulsions on storage. Silicone mixtures comprised of 25 pts. CSI Code C/75 pts. 8000 cs. silanol fluid and 25 pts. CSI Code D/75 pts. 8000 silanol fluid were emulsified to 35% silicone actives as described in Example III and buffered with NaHCO<sub>3</sub>. These systems were stored at room temperature and were periodically observed for appearance and gas

chromatographically analyzed for free methanol content. The analytical results are displayed below.

Emulsion Stability Studies

5	Days Storage	25/75 CSI Code C/ Silanol	25/75 CSI Code D/ Silanol
		wt% Free MeOH	wt% Free MeOH
	1	0.005	0.026
10	14	0.005	0.046
	28	0.01	0.075
	84	0.005	0.065

15 At this point there was no change in the initial appearance of the emulsions and the tests were terminated. Additional methanol was generated by KOH treatment of the emulsions thus conclusively showing the surprising stability of methoxy  
20 endblockers in properly buffered emulsions.

Example VIII

As in Example IV this example illustrates durable dimensional stability and tear strength  
25 improvements for other CSI/silanol fluid systems at 1% silicone solids on 100% cotton knits. Example IV data was based on CSI having chain lengths of 112 dimethyl siloxy units and cured with BAP catalyst. This example was  $\text{Zn}(\text{NO}_3)_2$  catalyzed and  
30 containing CSI having chain lengths comprised of only 27 dimethyl siloxy units (relative to 112 dimethyl siloxy units for Example IV). The data in Table VI clearly show that after 3 washes the dimensional stability has been improved 50% (course  
35 and wale) and the wale tear strength has increased

15%. These enhancements have been achieved for silicone systems based on 1000-50,000 cs. silanol fluids when blended with 10-50 wt% CSI as per the model finishing bath formulation and cure conditions.

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TABLE VI  
100% Cotton, Single Knit

TREATMENTS (a)	DIMENSIONAL STABILITY, %		WETTABILITY, SECONDS		TEAR STRENGTH	
	Course	Wale	INITIAL	3 WASHES	Course	Wale
As Rec'd Fabric	+17.1	-21.9	2	1	2300	2600
I) 15/85 - CSI Code A/Silanol Fluid						
Silanol Fluid visc.						
(1000) cs	+8.9	-11.2	4	2	2100	3100
(8000) cs	+7.8	-12.1	5	2	2200	3000
(20M) cs	+10.8	-11.3	6	2	2200	3000
(50M) cs	+7.7	-11.4	9	3	2100	2900
II) 15/85 - CSI Code B/Silanol Fluid						
Silanol Fluid visc.						
(1000) cs	+10.1	-12.2	300	300	2200	3000
(8000) cs	+12.4	-12.1	300	164	2200	3000
(20M) cs	+13.3	-13.3	300	300	2200	3000
(50M) cs	+11.4	-12.0	300	300	2100	3000
III) CSI Code B/Silanol (8000 cs) Blends						
10/90	+9.9	-12.1	63	3	2200	3100
15/85	+12.4	-12.1	300	164	2200	3000
25/75	+8.7	-12.0	55	24	2100	3100
50/50	+9.3	-11.8	300	300	2100	3000

Notes: a) Finishing Bath Formulations 1% Silicone Solids (BOWF)

	Parts by Weight	
	2.9	---
CSI/Silanol (350)	0.4	---
Zn(NO <sub>3</sub> ) <sub>2</sub> Cat. (25%)	96.7	95.6
Distilled Water		

b) Fabric Wet Pick-Up: 120%  
c) Dry/Cure: 11/2 min @171°C

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Experimental IX

5 This example is illustrative of the broad applicability of imparting durable dimensional stability and tear strength improvements for wide ranging CSI/silanol emulsion systems applied and cured into 50/50 polyester/cotton knits. Here tested were the same silicone formulae employed in Example VIII using  $\text{Zn}(\text{NO}_3)_2$  as the curing catalyst. Table VII shows the composition of the specific treating systems, the weight fabric wet pick up to provide 1% silicone solids, and the cure conditions. Again the data in Table VII clearly show that after 3 washes the course and wale tear strength was improved 25-30% and there was 15-20% improvement in dimensional stability.

10

15

Similar improvements were achieved using 1% BAP catalyst.

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Table VII  
50/50 Polyester Cotton Knit

TEAR  
GRAMS,  
Course

STRENGTH  
3 WASHES  
Wale

DIMENSIONAL  
STABILITY, %  
3 WASHES  
Wale

TREATMENTS (a)

As Rec'd Fabric

I) 15/85 = CSI Code A/Silanol Fluid

Silanol Fluid Visc.

(1000) cs  
(8000) cs  
(20H) cs  
(50H) cs

II) 15/85 = CSI Code B/L9000

Silanol Fluid Visc.

(1000) cs  
(8000) cs  
(20H) cs  
(50H) cs

III) CSI Code B/Silanol (8000) Blends

10/90  
15/85  
25/75  
50/50

Notes: a) Finishing Bath Formulations  
1% Silicone Solids (BWP)

b) Experimental Emulsions

Parts by Weight

Parts by Weight

Experimental Silicon Emulsion (35%)  
Zn(NO<sub>3</sub>)<sub>2</sub> Cat., (25%)  
Distilled Water

Silicone Fluid 35.00  
Nonionic Emulsifier 1.75  
Water 63.0  
Preservative 0.10  
NaHCO<sub>3</sub> 0.05

c) Dry/Cure Cycle: 11/2 min @ 171°C  
d) Fabric Wet Pick-up: 119%

Example X

This example is illustrative of 50/50 polyester cotton knit treated with a durable press resin bath to which CSI/silanol fluid emulsion compositions have been added. The results clearly show the entire bath treating system has improved physical properties as well as imparting a desirable soft hand relative to the fabric as received and containing resin alone. Thus both CSI containing on average 27 dimethyl siloxy units and endblocked with dimethoxy or tetramethoxy clusters were blended with 1,000 to 50,000 cs. silanol fluids and after emulsification, directly added to the durable press bath, co-cured with the durable press resin system without additional catalyst. In addition, these silicone emulsion compositions can contain 10 - 50 wt% CSI solids, the balance being comprised of silanol fluids.

The data in Table VIII shows durable dimensional stability has been improved 50% in both wale and course directions and the tear strength improved 30-40% relative to the untreated fabric. Relative to the 50/50 knit treated with resin only, there are dramatic improvements in both softness and physical properties which are required for the fabric to be commercially acceptable.



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Table VIII  
50/50 Polyester Cotton Knit Finished with DP Resin/CSI/Silanol Systems

TREATMENTS-	DIMENSIONAL STABILITY, %		TEAR GRAMS, Course	STRENGTH 3 WASHES Male
	Course	Male		
As Rec'd Fabric	-1.4	-10.3	1700	2100
Resin Only	+0.9	-5.2	2000	1300
I) 15/85 = CSI Code A/Silanol Fluids				
Silanol Fluid Visc.				
(1000) cs	0.0	-4.8	2000	2800
(8000) cs	+0.9	-4.8	2100	2800
(20M) cs	+0.6	-4.4	1800	2700
(50M) cs	+0.2	-4.7	2000	2800
II) 15/85 = CSI Code B/Silanol Fluids				
(1000) cs	+0.8	-5.0	2300	2800
(8000) cs	+0.5	-4.9	2000	2700
(20M) cs	0.0	-5.2	2000	2900
(50M) cs	+1.1	-5.2	2100	2800
III) CSI Code B/Silanol (8000)( cps blends				
mPa.s				
10/90	+0.6	-5.0	2200	2700
15/85	+0.5	-4.9	2200	2700
25/75	+0.5	-4.9	2100	2800
50/50	+0.2	-5.5	2000	2700
Notes: A) Finishing Bath Formulations				
Parts by Weight		Dry/Cure Cycle:		
Commercial Durable Press Resin (40%)		11/2 min @ 171°C		
Zn(NO <sub>3</sub> ) <sub>2</sub> (25%)		C) Fabric Wet		
Experimental Silicone Emulsion (35%)		Pick-Up: 125%		
Water		D) Silicone loading: 1% solids BOMF		
		2.3		
		81.6		

Example XI

The properties of 65/35 polyester/cotton woven fabric, Type 190, ( $3^{102} \text{ oz/yd}^2$ ) were improved by treatment with a durable press finishing bath containing CSI/silanol compounds as a elastomeric softener component. Table IX lists the durable dimensional stability provided by the resin/silicon softener system relative to the as received fabric and the 100% improvements in durable tear strength relative to the durable press treated fabric alone. Illustrated in this example are the utility of 2,000 - 2,500 mol. weight dimethoxy and tetramethoxy endblocked silicone fluids admixed with 1,000-50,000 cs. silanol fluids which were added to the treating bath as concentrated emulsions. The wt% polymethoxy endblocked silicone compounds co-cured with the durable press resin without the need for additional catalyst.

The tear strength of the silicone treated fabric was doubled in both the fill and warp directions. The hand was soft, smooth, and lively relative to the durable press resin treatment alone. These properties are required for fabric to be of commercial utility.

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Table IX  
65/35 Polyester-Cotton Woven Fabric Treated with DP Resin/PHEBS/Silanol

TREATMENTS	DIMENSIONAL STABILITY, % 3 WASHES	TEAR GRAMS, FILL	STRENGTH 3 WASHES WARP
As Rec'd Fabric	-1.3	-3.0	----
Resin Only	0.0	-0.8	700 600
I) 15/85 - CBI Code A/Silanol Fluids			
Silanol Fluid Visc.			
(1000) cP	-0.5	-1.0	1400 1100
(8000) cP	-0.5	-1.0	1500 1200
(20M) cP	-0.5	-1.0	1600 1100
(50M) cP	-0.5	-1.0	1500 1200
II) 15/85 - CBI Code B/Silanol Fluids			
(1000) cP	-0.5	-1.0	1400 1100
(8000) cP	-0.5	-1.0	1400 1200
(20M) cP	-0.5	-1.0	1500 1200
(50M) cP	-0.5	-1.0	1500 1200
III) CBI Code B/Silanol (8000) (cps), silanda			
10/90	-0.5	-1.0	1400 1200
15/85	-0.5	-1.0	1400 1200
25/75	-0.5	-1.0	1500 1200
50/50	-0.5	-1.0	1400 1100

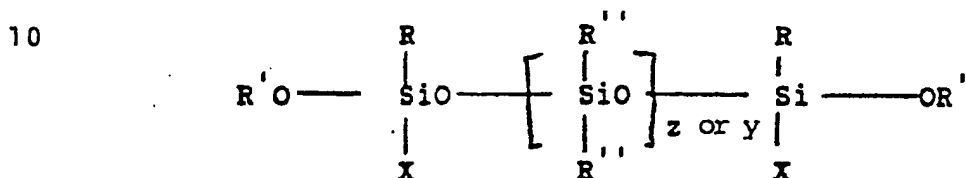
Notes: A) Finishing Bath Formulations	Parts by Weight	B) Fabric Wet
Commercial Durable Press Resin (40%)	14.0	Pict-Up 125a
3a(NO3)2 (25%)	2.1	Dry/Cure Cycle:
Experimental Silicone Emulsion (35%)	2.3	1 1/2 min @ 171°C
Water	81.6	1b Silicone Solids
		(BOWP)

CLAIMS

1. A process for imparting an lastomeric finish to a substrate which comprises:

(a) applying to said substrate a silicone blend comprising:

5 (1) a crosslinkable silicone intermediate selected from the group of silicone compositions of the general formula:



15 wherein R is individually hydrogen, OR' or a substituted or unsubstituted hydrocarbon radical containing from 1 to 12 carbon atoms;

R' is individually a hydrocarbon radical containing from 1 to 6 carbon atoms;

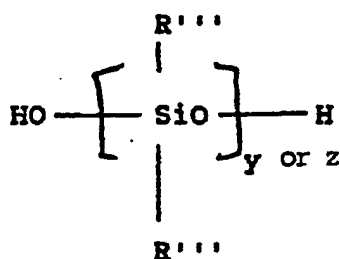
and X is either R, OR' or

20  $(\text{C}_n\text{H}_{2n}\text{Si}(\text{R})_a(\text{OR}')_{3-a})$  wherein n is 1, 2 or 3 and a is 0, 1 or 2;

z has a value from 10 to 500; and R'' is individually a hydrocarbon radical

25 containing from 1 to 12 carbon atoms and may be cyclic or noncyclic, branched or nonbranched, substituted or unsubstituted, or saturated or unsaturated and

(2) a silanol selected from the group of silanols of the general formula:



5                    wherein R''' is individually a hydrocarbon  
radical containing from 1 to 12 carbon  
atoms and may be cyclic or noncyclic,  
branched or unbranched, substituted or  
unsubstituted or saturated or unsaturated  
10                   and y has a value of from 185 to 3500; and

(B) catalyzing and curing the  
silicone blend onto the substrate .

15                   2.    The process of claim 1 wherein the  
substrate is selected from the group consisting of  
textiles, paper, cellulose materials, glass fibers  
and mineral fibers.

20                   3.    The Process of claim 1 or 2 wherein the  
silicone blend is applied to said substrate in an  
amount from 0.1 to 10 parts by weight per 100 parts  
by weight of untreated substrate.

25                   4.    The process of claim 1 wherein R is  
hydrogen or methyl group.

5.    The process of claims 1 to 4 wherein  
R' is a hydrocarbon radical containing from 1 to 3  
carbon atoms, preferably methyl.

6.    The process of claims 1 to 5 wherein  
R'' is methyl.

7. The process of claims 1 to 6 wherein X is R or OR' or  $(C_2H_4)Si(OR')_3$  or  $(C_2H_4)Si(R)(OR')_2$ .

8. The process of claims 1 to 7 wherein z has a value of from 15 to 150.

9. The process of claims 1 to 8 wherein R''' is methyl.

10. The process of claims 1 to 9 wherein y is 750 to 3500.

11. The process of claim 1 wherein the cross-linkable silicone composition is:

15

